Mesoporous Amine-bridged Polysilsesquioxane for CO_2 Capture

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Abstract: a novel class of amine-supported sorbents based on amine-bridged mesoporous polysilsesquioxane was developed via a simple one-pot sol-gel process. The new sorbent allows the incorporation of a large amount of active groups without sacrificing surface area or pore volume available for CO_2 capture, leading to a CO_2 capture capacity of 3.2 mmol g^{-1} under simulated flue gas conditions. The sorbent is readily regenerated at 100 °C and exhibits good stability over repetitive adsorption-desorption cycling.

Key words: Carbon dioxide capture; polysilsesquioxane; mesoporous; sorbent; post-combustion

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Post-combustion capture is believed to be the most feasible near-term solution to mitigate surging carbon dioxide emissions, which has been widely assumed to be a cause for global climate change.[1] Despite the proved efficiency of post-combustion CO_2 capture, the current state-of-art process, amine scrubbing, is energy-intensive and requires the use of capital-intensive equipment.[2] To overcome these challenges, adsorption via solid-supported amines has been developed as an alternative approach for CO_2 capture.[3] Taking advantage of the reversible amine-CO_2 chemistry similar to that in amine scrubbing process, solid-supported amine sorbents can separate CO_2 from dilute flue gases with a high selectivity. Meanwhile, their toxicity, corrosivity and associated energy penalty required for sorbent regeneration can be significantly reduced since the amines are anchored to solid supports. Furthermore, unlike zeolites, carbonaceous adsorbents and certain metal-organic frameworks which rely mainly on physisorption, solid amine-functionalized sorbents are more robust to moisture, making them promising candidates for post-combustion CO_2 capture.[3]

Most of advanced amine-supported sorbents up to now have been synthesized by the immobilization of amines into mesoporous supports via one of the following strategies: post-grafting, wet impregnation and cocondensation of aminosilanes and tetraalkoxysilanes.[3-22] Although sorbents with relatively high amine loadings can be achieved, post-grafting and wet impregnation involve multi-step synthesis in which the supporting materials are separately prepared. In addition, the increase of amine content of the sorbents comes usually at the expense of surface area and pore volume available for CO_2 capture ultimately compromising the performance of the sorbents. In contrast to post-grafting and wet impregnation, the approach based on cocondensation is more

straightforward and amine groups can be directly introduced into the sorbents by simply using the appropriate silane precursors. However, as the hydrolysis and condensation rates of silane monomers are different and amine groups tend to disrupt the formation of ordered mesoporous networks, only a limited amount of amine functionalities can be incorporated into the sorbents.

In this paper, we report a novel class of amine-supported sorbents based on mesoporous amine-bridged polysilsesquioxane. Our approach is different from those mentioned above in that the new sorbent was prepared via a simple one-pot sol-gel process, using solely a single silica precursor, N, N'-Bis-[3-(trimethoxysilyl) propyl]-ethylenediamine (TMSEN). Because the amine groups are integrated into the framework of the sorbent instead of grafted in the mesopores, the challenges rooted in post-grafting or wet impregnation, such as loss of surface area, pore blocking and nonuniform amine distribution after amine functionalization, are largely overcomed.

In a typical procedure, as shown in Scheme 1, a solution of deionized water (1.2 g) and methanol (1.0 g) was added to a homogenous mixture of the surfactant, a triblock copolymer poly(ethylene glycol)-b-poly(propylene glycol)-b-poly(ethylene glycol) (P123, 5 g), and the monomer (TMSEN, 5 g) at 5 ^{o}C under vigorous stirring. The derived gel was aged for 24 h at 40 ºC and for another 48 h at 70 ºC, followed by extraction with methanol to remove the surfactant and drying under vacuum at room temperature for 12 hours.

As no tetraalkoxysilanes are used in the synthesis, the amine content in the polysilsesquioxane sorbent is much higher from those prepared via the cocondesation approach using TMSEN as a comonomer. Thermogravimetric analysis of the sorbent

(Fig. S1) shows a significant weight loss (more than 50 %) in the temperature range of 300-600 °C, which mainly corresponds to the decomposition of the bridging groups. Because of the high surface area of the sorbent (see Fig. S2) a large number of amine groups are accessible to CO_2 instead of being trapped in the matrix, which helps to improve the CO_2 capture efficiency. Therefore, efforts have been devoted to developing high surface area polysilsesquioxanes from amine-bridged silanes but with limited success. Burleigh et al. and Tang et al. prepared poly(TMSEN)s in emulsions using either cationic or anionic surfactant templates.[19, 23] Unfortunately, they obtained materials with relatively low porosity (BET surface area ~ 30 - 40 m^2g^{-1}). The low surface area has been attributed to the lack of rigid spacers in TMSEN to form robust mesoporous structures. The fast gelation rate of TMSEN brings additional challenges for the preparation of mesoporous poly(TMSEN).[24] To overcome such challenges, a concentrated P123 solution was used in our synthesis. The low concentration of water enables TMSEN to nucleate into extremely small nanoparticles at a moderate rate. According to the TEM image in Fig. 1a, the sorbent is made of aggregates of partially fused nanoparticles with a size ranging mainly from 5 to 10 nm, suggesting that the "controlled aggregation" mechanism may play an important role in the growth of these nanoparticles.[24] In contrast to the xerogel nanoparticles of poly(TMSEN) prepared in the water-in-oil emulsion,[24] a highly porous monolith was obtained with our approach, as shown in Fig. 1b. The walls of the interstitial voids between the nanoparticles are robust enough so that high porosity is maintained after the removal of the surfactant.

The nitrogen physisorption of the sorbent follows type IV isotherm according to the IUPAC classification (Fig. S2). A hysteresis loop is present at relative pressures of 0.7-

0.95. The calculated BET surface area is 448 m^2g^{-1} and the average pore size is 13.8 nm based on Barrett-Joyner-Halenda (BJH) model. No significant structure is observed in the XRD pattern (Fig. S3), which implies that the pores in the sorbent do not possess any long-range order, consistent with the morphology in the TEM image (Fig. 1a).

The ATR FT-IR and the NMR spectra confirm the covalent integration of the bridging amine functionalities in the sorbent. Fig. 2 shows the ATR FT-IR spectrum of the sorbent recorded under vacuum. The strong absorptions between 1150 and 1000 cm^{-1} are due to Si-O-Si stretching vibrations. [25, 26] The broad bands at 1980 and 1850 cm^{-1} are overtone vibrations of Si-O-Si groups.[27] The absorption at 932 cm^{-1} can be attributed to the stretching vibration of Si-OH.[25] The bands at 3300, 1595 and 770 cm^{-1} correspond to the symmetric stretching, deformation and wagging vibration of N-H, respectively.[25, 28] The absorption at 1660 cm^{-1} is due to deformation of the protonated amino groups $R\text{-}NH_3^+ \cdots {}^-O\text{-}Si$.[27] Peaks at 2930, 2880, 2810, 1460, 1410, 1346, and 1276 cm^{-1} are due to the vibrations of methylene groups in the bridging spacer. [28, 29] The absorption band at 690 cm^{-1} can be assigned to the $Si\text{-}CH_2$ stretching.[26] The broad band at 2160 cm^{-1} could be due to vibrations of NH_3^+ groups, according to the assignment by Bacsil et al.[30] Fig. S4a shows the qualitative ^{29}Si MAS NMR spectrum of the sorbent. A dominant peak at 57.9 ppm corresponds to the T2 structure ($CSi(OH)(OSi)_2$).[26, 31] The small shoulder around 49.0 ppm can be ascribed to the T1 ($CSi(OH)_2(OSi)$) silicon sites.[31] The absence of signal corresponding to Q sites in the range of 90 to 110 ppm indicates that there is no cleavage of Si-C bonds during the synthesis of the sorbent.[26, 31] The ^{13}C CPMAS NMR spectrum of poly(TMSEN) is shown in Fig. S4b. The resonances at 10.4, 23.3, and 50.4 ppm can be assigned to the carbon species C1, C2 and C3 of $Si\text{-}CH_2(C1)\text{-}CH_2(C2)\text{-}CH_2(C3)\text{-}NH$-

CH_2(C3)-CH_2(C3)-NH-CH_2(C3)-CH_2(C2)-CH_2(C1)-Si. No significant signal was observed at 72.1 ppm, where the chemical shift of potential P123 residue is typically seen, suggesting that most of the surfactant was removed by the solvent extraction.[32]

The adsorption kinetics of the sorbent was investigated gravimetrically in dry 100% and 10% CO_2 (balanced with N_2) at 25 ^oC under ambient pressure. As shown in Fig. 3, both systems show a two-stage adsorption. When dry 100% CO_2 was used, a sharp linear weight gain occurs once the sorbent was exposed to the CO_2 stream. The corresponding CO_2 capacity after one minute is ~ 2.1 mmol g^{-1}. The steep rise is followed by a much slower adsorption process with the sorbent reaching a capacity of ~ 2.6 mmol g^{-1} after 60 min. When dry 10% CO_2 was used, the adsorption kinetics followed a similar trend except that the capacity was slightly lower, ~ 2.2 mmol g^{-1} after 60 min. The two-stage adsorption behavior is typical of other amine-based solid sorbents [3, 4, 15] and has been attributed to CO_2 diffusion resistance in the sorbents. [3-5, 16] The adsorption kinetics of the sorbent was also investigated gravimetrically in simulated flue gas (prehumified 10% CO_2) at 25 ^oC under ambient pressure. The activated sorbent was first equilibrated in the pre-humified N_2 at 25 ^oC for 4 h. A weight gain of ~ 8 wt % was attributed to the adsorption of moisture (see Fig. S5). The gas was then switched to the pre-humified 10% CO_2 at 25 ^oC. A similar adsorption behavior is seen under simulated flue gas conditions except that the kinetics are slightly slower during the first stage but the overall capture capacity is much higher. The adsorption capacity of the sorbent reaches ~ 3.2 mmol g^{-1} (based on the dry weight of the sorbent) after 60 min, which is among the highest reported for solid sorbents with covalently bonded amines.[3] The positive effect of moisture on the capacity of amine functionalized sorbents has been contributed to the

formation of bicarbonate in the presence of moisture.[13, 14, 33, 34]

The effect of the adsorption temperature on capture capacity was investigated using 1 atm dry CO_2. As shown in Fig. 4, the capacity decreases significantly from 2.6 to 0.3 mmol g^{-1} as the temperature increases from 25 to 80 ^oC. The drastic decrease of the capacity and the relatively small temperature differential for adsorption/desorption (see adsorption-desorption cyclic runs below) are very beneficial for minimizing the energy penalty for sorbent regeneration.

The long-term stability of the sorbent over multiple adsorption/desorption cycles is critical for practical applications. To that end, a modified temperature swing was used to evaluate the stability of the sorbent. In a typical cycle, the activated sorbent was first exposed to 1 atm dry 100% CO_2 (40 ml min^{-1}) at 25 ^oC for 30 min. The gas was then switched from CO_2 to N_2 (40 ml min^{-1}) and the temperature was ramped to 100 ^oC at a rate of 10 ^oC min^{-1}. After 10 min holding time to regenerate the sorbent, the temperature was decreased to 25 ^oC and held for another 5 min prior to the next cycle. In the cyclic test, the sorbent showed a rapid desorption rate which was completed within ~15 min. As shown in Fig. 5, no loss of CO_2 capacity was observed after 10 adsorption-desorption cycles.

In summary, a novel class of amine-supported sorbent based on mesoporous amine-bridged polysilsesquioxanes was developed via a simple one-pot sol-gel process. The sorbent exhibits a type IV isotherm with a calculated BET surface area of 448 m^2g^{-1} and an average pore size of 13.8 nm but the mesopores lack any significant long-range order structure. The ATR FT-IR and NMR data confirm that the sorbent is based on an amine-bridged polysilsesquioxane and no degradation of the bridging groups occurs during the

synthesis. The sorbent exhibits fast CO_2 capture kinetics (adsorption of 2.1 mmol g^{-1} after about one minute in 1 atm dry 100% CO_2 at 25^{o}C) and reaches a capture capacity after 60 min of 2.6 and 3.2 mmol g^{-1} under 1 atm dry CO_2 and simulated flue gas conditions, respectively. In addition to the high capture capacity the sorbent can be fully and quickly regenerated (within 5 min) at relatively low temperatures (~ 100 ^{o}C) and exhibits good stability over repetitive adsorption-desorption cycling.

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Supporting Information Available: Experimental details of the synthesis and characterization of the sorbent. Adsorption and desorption of the sorbent.

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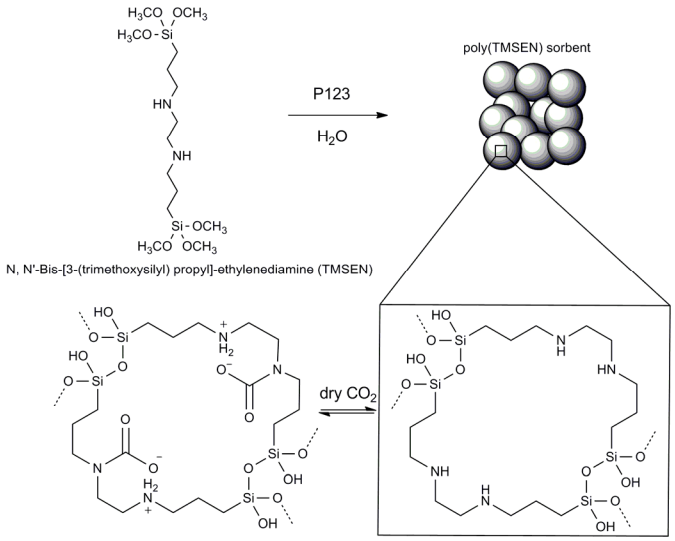

Scheme 1. Schematic synthesis of the poly(TMSEN) sorbent .

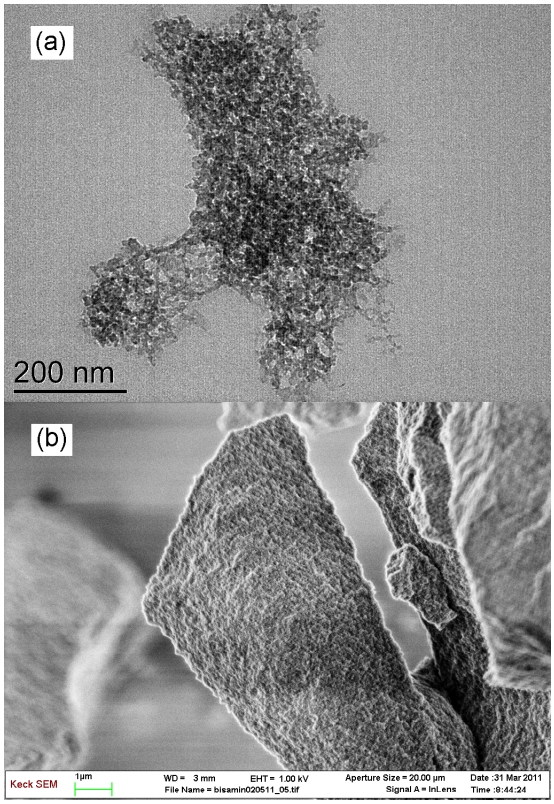

Figure 1. Transmission electron micrograph (a) and scanning electron micrograph (b) of the poly(TMSEN) sorbent.

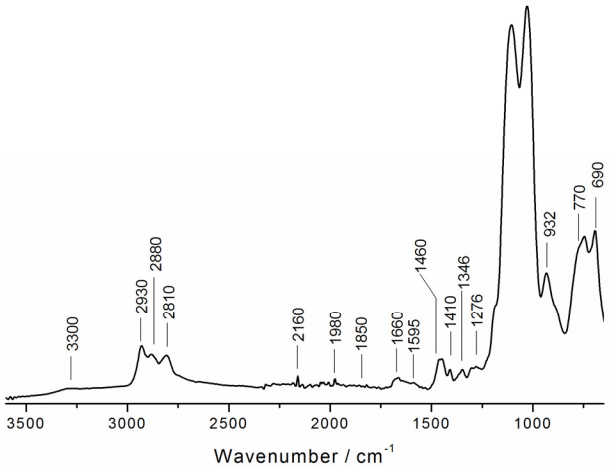

Figure 2. ATR FT-IR spectrum of the mesoporous poly(TMSEN) sorbent.

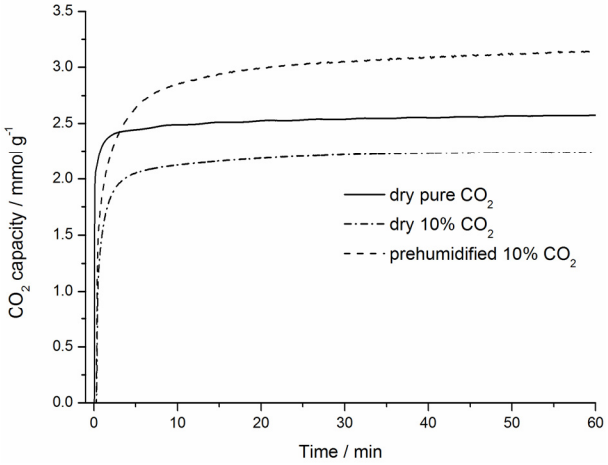

Figure 3. CO_2 capture kinetics of the mesoporous poly(TMSEN) sorbent. The adsorption was measured at 25 ^{o}C.

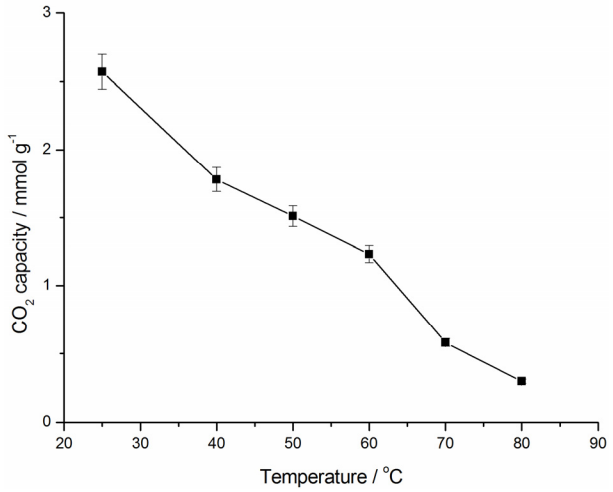

Figure 4. CO_2 capacity of the poly(TMSEN) sorbent at different temperatures. The CO_2 capacity was measured under 1 atm dried CO_2 for 60 min.

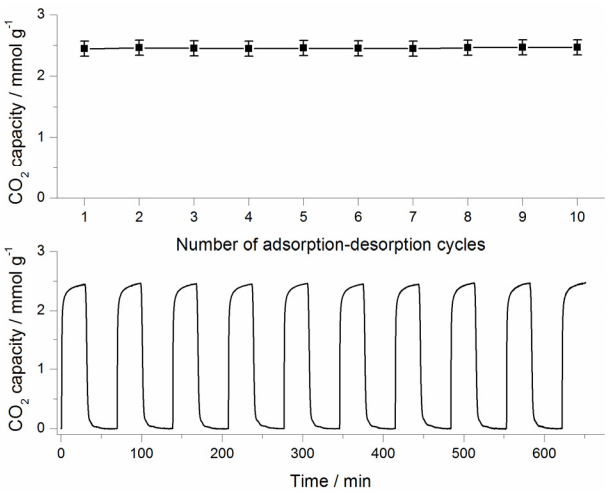

Figure 5. CO_2 capacity of the poly(TMSEN) sorbent over multiple adsorption-desorption cycles.